

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 363 147  
A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 89310092.5

(51) Int. Cl.<sup>5</sup>: **G11B 9/00**

(22) Date of filing: 03.10.89

(30) Priority: 04.10.88 JP 251455/88  
01.12.88 JP 302223/88

(43) Date of publication of application:  
11.04.90 Bulletin 90/15

(84) Designated Contracting States:  
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: **CANON KABUSHIKI KAISHA**  
30-2, 3-chome, Shimomaruko  
Ohta-ku Tokyo(JP)

(72) Inventor: **Kawada, Haruki**  
48-1-1-208, Kamadai Hodogaya-ku  
Yokohama-shi Kanagawa-ken(JP)  
Inventor: **Matsuda, Hiroshi**  
17-2, Higashi Naruse Isehara-shi  
Kanagawa-ken(JP)  
Inventor: **Takimoto Kiyoshi**  
2-13-202, Kuriya 4-chome Tama-ku  
Kawasaki-shi Kanagawa-ken(JP)  
Inventor: **Nose, Hiroyasu**  
4731-1-204, Sobudai 3-chome Zama-shi  
Kanagawa-ken(JP)

(74) Representative: **Beresford, Keith Denis Lewis**  
et al  
**BERESFORD & Co.** 2-5 Warwick Court High  
Holborn  
London WC1R 5DJ(GB)

(54) **Recording and reproducing apparatus and recording and reproducing method and recording medium for the recording and reproducing method.**

(57) A recording-reproducing apparatus, comprising a material, in which an intramolecular electron distribution can be changed, by electromagnetic wave irradiation and electric field application, a probe electrode brought close to the material, a means for projecting an electromagnetic wave onto the material, and a means for applying an electric field between the material and the probe electrode, is provided.

**EP 0 363 147 A2**

# Recording and Reproducing Apparatus and Recording and Reproducing Method and Recording Medium for the Recording and Reproducing Method

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to a recording-reproducing apparatus for recording by employing electromagnetic wave irradiation and electric field application and reproducing by detecting a tunnel current, and a recording-reproducing method employing the apparatus. And the present invention relates to further a novel recording medium used suitably for the recording and reproducing method.

### Related Background Art

Applications of memory materials are the most important field of electronic industries such as computers and related apparatus, video-disks, and digital audio-disks. The development of the materials are the subject of comprehensive studies in recent years. Although the performances required to the memory materials depend on the application fields thereof, the generally required performances are as below:

- (1) High recording density and large recording capacity.
- (2) High response speed of recording and reproduction,
- (3) Low electric power consumption, and
- (4) High productivity and low cost. and so forth.

Heretofore, semiconductor memories and magnetic memories based on a semiconductor or a magnetic substance are predominantly used for memory materials. Lately as a result of the progress of laser technology, low-cost and high-density recording media have been developed employing an optical memory by use of an organic thin film of an organic coloring matter, a photopolymer, etc.

On the other hand, the scanning tunnelling microscope (hereinafter referred to as STM) has been recently developed to enable a direct observation of an electronic structure of surface atoms or molecules of a conductor with a resolving power of 0.1 nm [G. Binnig et al., Phys. Rev. Lett. 49 (1982) 57]. Recently, by using STM, an experiment has been conducted in which a pulse voltage is applied between a probe electrode and an electroconductive material to fabricate locally the surface of the electroconductive material and the change of the shape or state of the surface is read [J. S. Foster et al., Nature 331 (1988) 324]. Further by means of the STM, switching characteristics and rectification characteristics of an organic molecule have been investigated [A. Aviram et al., Chem. Phys. Lett. 146 (1988), 490].

However, even with the highest density and the largest recording capacity of the conventional optical memories practically used, the recording capacity is at most  $10^8$  bit/cm<sup>2</sup>, which is becoming insufficient to the image recording in modern computers and video apparatuses.

The recording and reproduction by use of STM, although the recording can be conducted with a bit size in the order of an interatomic or intermolecule distance (0.5 to 50 nm), is not satisfactory from the viewpoint of the reproductivity and stability, and yet its recording and erasing mechanism has not been elucidated. Moreover, in measurement of electric characteristics by accessing a molecule by means of STM, the record may sometimes be affected by reproducing operation (voltage application) because recording and reproduction are made by voltage application. Therefore STM is not satisfactory for application to memory.

## SUMMARY OF THE INVENTION

The object of the present invention is to provide a recording-reproducing apparatus satisfactory in reproductivity and stability of recording, and has a large recording capacity, and also to provide a method for recording and reproducing employing the apparatus. And the object of the present invention is to provide a novel recording medium used suitably for the recording and reproducing method.

The above object is achieved by the present invention described below.

According to an aspect of the present invention, there is provided a recording-reproducing apparatus, comprising a material, in which intramolecular electron distribution can be changed, by electromagnetic

irradiation and electric field application, a probe electrode brought close to the material, a means for projecting an electromagnetic wave onto the material, and a means for applying an electric field between the material and the probe electrode.

According to another aspect of the present invention, there is provided a recording-reproducing apparatus, comprising a recording, in which a material selected from the group of compounds consisting of  
 5 azo compounds, styrene derivatives and imino compounds having a quinone group and hydroquinone group in the molecule, and azo compounds, styrene derivatives and imino compounds having two amino groups in the molecule is deposited on an electrode; a probe electrode brought close to the recording medium; a means for projecting an electromagnetic wave onto the recording medium; and a means for applying  
 10 electric field between the recording medium and the probe electrode.

According to still another aspect of the present invention, there is provided a recording-reproducing apparatus, comprising a recording medium in which a charge transfer complex is deposited on an electrode, a probe electrode brought close to the recording medium, a means for projecting light onto the recording medium, and a means for applying electric field between the recording medium and the probe  
 15 electrode.

According to a further aspect of the present invention, there is provided a recording method comprising projecting an electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application to cause change in the electron distribution in the molecule of the material to write information,  
 20 thereby conducting information-recording.

According to a still further aspect of the present invention, there is provided a recording-reproducing method, comprising conducting information-recording by projecting an electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application thereby causing change in the electron  
 25 distribution in the molecule of the material to write information; and conducting information readout by detecting a tunnel current at the portion where the information is recorded.

According to a still further aspect of the present invention, there is provided a recording-reproducing-erasing method, comprising conducting information-recording by projecting an electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be  
 30 changed, by electromagnetic wave projection and electric field application thereby causing change in the electron distribution in the molecule of the material to write information; conducting information readout by detecting a tunnel current at the portion where the information is recorded; and erasing the information by projecting an electromagnetic wave and simultaneously applying electric field onto the portion where the information is recorded.

According to still further aspect of the present invention, there is provided a recording-reproducing-erasing method, comprising conducting information-recording by projecting an electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be  
 35 changed, by electromagnetic wave projection and electric field application thereby causing change in the electron distribution in the molecule of the material to write information; conducting information readout by detecting a tunnel current at the portion where the information is recorded; and erasing the information by  
 40 introducing a vibration energy to the portion where the information is recorded.

According to still further aspect of the present invention, there is provided a recording medium, comprising providing a material capable of causing a proton-transfer by photoisomerization on a substrate.

#### 45 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a block constitution of the embodiment of a recording-reproducing apparatus of the present invention.

50 Fig. 2 illustrates a block constitution of another embodiment of a recording-reproducing apparatus of the present invention.

Fig. 3 illustrates an example of the signal in recording operation.

Fig. 4 illustrates an example of the signal in erasing operation.

Fig. 5 shows the principle of recording by memory materials.

55 Fig. 6 shows a memory material and the principle of erasing therewith.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is described in detail below.

The materials employed in the present invention are those, in which an electron distribution in the molecule can be changed, by irradiation of an electromagnetic wave and application of voltage.

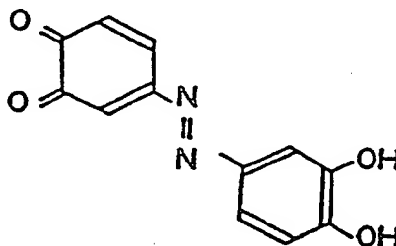
Embodiment of the materials includes

(1) memory materials, in which a redox pair (an oxidation-reduction pair) within the molecule or between the molecules is formed due to isomerization in the molecular structure by electromagnetic wave irradiation, and an electron distribution in the molecule is changed due to proton transfer in the redox pair by further electric field application, and

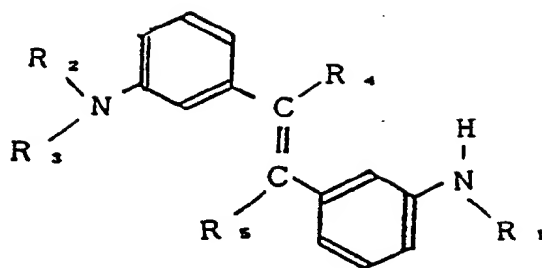
(2) memory materials, in which an molecular distribution in the molecule is changed, by irradiation with electromagnetic wave and simultaneous application of an electric voltage exceeding the threshold voltage for causing memory effect.

Embodiment (1) of the memory materials includes specifically azo compounds having a quinone group and a hydroquinone group within the molecule, styrene derivatives having a quinone group and a hydroquinone group within the molecule, imino compounds having a quinone group and a hydroquinone group within the molecule, azo compounds having two amino groups within the molecule, styrene derivatives having two amino groups within the molecule, and imino compounds having two amino groups within the molecule. Examples of the preferred compounds are shown below:

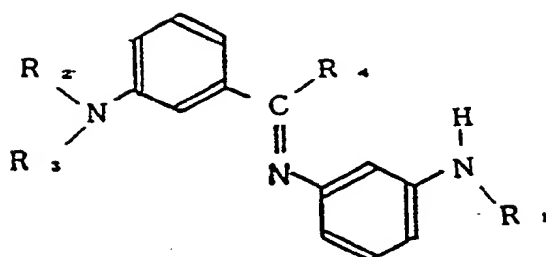
No. 1



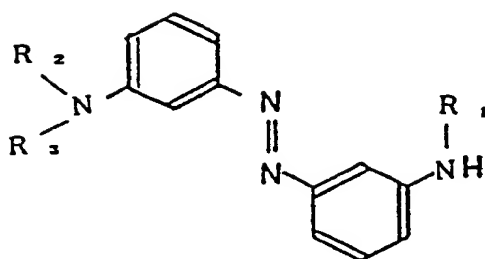
No. 2



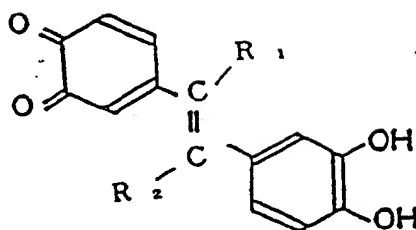
No. 3



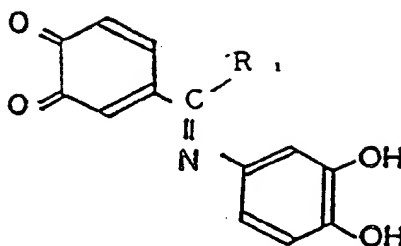
No. 4



No. 5



No. 6



(In the formulae,  $R_1 - R_5$  are  $CH_3$ ,  $C_2H_5$ , or isopropyl, and the positions of  $=O$ , or  $-OH$  are in the relation of ortho, meta, or para positions.)

Compounds of Nos. 1, 2, 4 and 5 among them are particularly preferred because of a high photoisomerization efficiency.

By use of these materials, the recording/reproducing/erasing are conducted as follows.

The electromagnetic wave irradiation onto the material causes isomerization in the molecular structure, forming a redox pair in the molecule, and further application of voltage causes proton transfer within the redox pair, resulting in change in intramolecular electron distribution into the recorded state of the present invention.

Erasing is conducted by irradiation of electromagnetic wave onto the recorded portion and simultaneous application of electric field in the reverse direction to cause reversed proton transfer.

In a non-irradiated state, application of an electric field onto the material does not cause the proton transfer and the resulting change of intramolecular electron distribution since no redox pair is present. Thus, in the memory material employed here, recording and erasing can be conducted by voltage application only under irradiation of an electromagnetic wave. In reproduction, since the material is not irradiated, no change occurs in recorded and erased states by application of an electric field between the memory material and the probe for tunnel current detection.

Embodiment (2) of the memory materials includes charge transfer complexes of a metal with an organic electron acceptor. Specific examples are, for example, n-octadecyltetracyanoquinodimethan copper complex (ODTCNQ/Cu), n-dodecyltetracyanoquinodimethan copper complex (DDTCNQ/Cu), n-octadecyltetracyanoquinodimethan silver complex (ODTCNQ/Ag), n-dodecyltetracyanoquinodimethan silver complex (DDTCNQ/Ag), and their derivatives.

By employing these materials, the recording/reproduction/erasing are conducted as follows.

Recording is conducted by applying to a probe electrode a voltage exceeding a threshold voltage for giving a memory effect corresponding to the information while irradiating an electromagnetic wave (or light); reproduction is conducted by applying a voltage to the probe electrode, and scanning the material with the probe electrode keeping a constant distance between the material and the probe electrode, and detecting the change of intensity of current flowing the probe electrode; and erasing is conducted by introducing vibration energy to the material.

Such memory material is used by depositing it on an electrode material.

As the electrode material, any material may be used which is capable of forming a film having



electroconductivity and smoothness. Examples of suitable materials are Au/Pd, Pt,  $n^+$ -Si, ITO, etc.

A preferable method for depositing a memory material onto an electrode is the Langmuir-Blodgett process in view of easiness of formation of a uniform, and defectless thin film with high regularity.

For projecting an electromagnetic wave onto the memory material, any electromagnetic wave source  
 5 may be employed which emits a light having a wavelength of from visible to infrared regions. Various light sources can be used as desired such as a xenon lamp, a helium-neon laser, an argon laser, a semiconductor laser, and carbon dioxide laser. The application voltage may be varied in connection with the light intensity.

Fig. 1 illustrates a block constitution of a recording apparatus of the present invention, where the  
 10 numeral 5 denotes a probe current amplifier; 6 denotes a servo circuit for controlling fine adjusting mechanism 7 which employs a piezo-element to maintain the probe current constant; and 8 denotes a power source for applying a pulse voltage between probe electrode 2 and electrode 3 for recording/erasing.

On application of a pulse voltage, the probe current abruptly changes, so that servo circuit 6 controls the HOLD circuit to be in an ON state during the change to maintain the output voltage constant.

15 9 is an XY scan-driving circuit for controlling the movement of probe electrode 2 in the XY directions. 10 is a coarse adjusting mechanism and 11 is a coarse adjusting-driving circuit, which coarsely control the distance between probe electrode 2 and recording medium 1 so as to give a probe current of approximately  $10^{-9}$  A. These mechanisms are all subjected to central control of microcomputer 12. 13 is a display device. 14 is an XY stage. 15 and 16 are each an electromagnetic wave source.

20 Examples of the mechanical performances in movement control employing a piezo-element are shown below.

Range of fine movement control in the Z direction:

0.1 nm to 1 nm

Range of coarse movement control in the Z direction: 10 nm to 10 mm

25 Range of scanning in the XY directions:

0.1 nm to 1 nm

Tolerance in measurement and control:

less than 0.1 nm

The examples below are intended to illustrate specifically the present invention.

30

#### Example 1

Fig. 1 illustrates a recording-reproducing apparatus of the present invention. Probe electrode 2 is made  
 35 of platinum/rhodium. Probe electrode 2 is finely controlled by a piezo-element to keep the distance (Z) from the surface of recording layer 101 to maintain the current at a constant level. Fine movement control mechanism 7 is designed to control finely the movement of the probe electrode in the plane (XY) direction with retention of the distance Z. Probe electrode 2 is capable directly of recording, reproducing and erasing information. The recording medium is placed on XY stage 14 and can be moved to a desired position.

40 The film of octadecyltetracyanoquinodimethan copper complex (ODTCNQ/Cu) was formed in the following procedure. A solution of  $4 \times 10^{-6}$  M ODTCNQ/Cu in acetonitrile (ACN) was prepared. The solution was spread on pure water at 20°C, and the surface pressure was raised to 20 mN/m to form a monomolecular film on the surface of water. A glass substrate having a vapor-deposited gold/palladium (Au/Pd) film of 300 Å thick which had been previously immersed in the water phase was slowly pulled up at  
 45 a rate of 5 mm/min in the direction crossing the water surface with the surface pressure maintained constant to form a monomolecular film of ODTCNQ/Cu on the glass substrate having vapor-deposited Au/Pd. This was employed as recording medium 1.

The experiment on recording-reproducing-erasing was conducted by employing recording medium 1 having a monolayer LB film of the ODTCNQ/Cu. Firstly, recording medium 1 was placed on XY stage 14,  
 50 and probe electrode 2 was fixed at a visually determined position. The distance Z between probe electrode 2 and the surface of recording layer 101 was adjusted by applying the voltage of 3 V between Au/Pd electrode 3 and the probe and by monitoring the current. On application of voltage of +300 mV to probe electrode 2, the current was found to be not more than 1 pA.

After stopping an application of the voltage, the recording was conducted by irradiating a light to  
 55 recording medium 1 with xenon lamp 15 and by applying again a voltage of +5 V to probe electrode 2. The recording medium was found to have transferred to an ON state in which the electricity flowed well.

The light irradiation and the voltage application were stopped, and then at the same position, a voltage of +300 mV was applied to probe electrode 2 to reproduce the record. A current of 5 nA was found to flow

there, which shows the retention of the ON state, namely the retention of the record.

After stopping an application of a voltage argon laser 16 was projected onto the recorded portion and vibration energy was given thereto. The vibration energy shall mean here an electromagnetic wave having about one figure smaller energy amount than that of an electromagnetic wave used for recording. Thereafter at the same position, a voltage of +300 mV was applied again to probe electrode 2 to reproduce the record. A current of not more than 1 pA was found to flow, which shows the transition to an OFF state, namely erasure of the record.

## 10 Example 2

The recording-reproducing apparatus illustrated in Fig. 1 was employed in the same manner as in Example 1.

The film of dodecyltetracyanoquinodimethan copper complex (DDTCNQ/Cu) was formed in the following procedure. A solution of  $4 \times 10^{-6}$  M DDTCNQ/Cu in acetonitrile (ACN) was prepared. The solution was spread on pure water at 20 °C, and the surface pressure was raised to 20 mN/m to form a monomolecular film on the surface of water. A glass substrate having a vapor-deposited gold/palladium (Au/Pd) film of 300 Å thick which had been previously immersed in the water phase was slowly pulled up at a rate of 5 mm/min in the direction crossing the water surface with the surface pressure maintained constant to form a monomolecular film of DDTCNQ/Cu on the glass substrate having vapor-deposited Au/Pd. This was employed as recording medium 1.

The experiment on recording-reproducing-erasing was conducted by employing recording medium 1 having a monolayer LB film of the DDTCNQ/Cu. Firstly, recording medium 1 was placed on XY stage 14, and probe electrode 2 was fixed at a visually determined position. The distance Z between probe electrode 2 and the surface of recording layer 101 was adjusted by applying the voltage of 3 V between Au/Pd electrode 3 and the probe and by monitoring the current. On application of voltage of +300 mV to probe electrode 2, the current was found to be not more than 1 pA.

After stopping an application of the voltage, the recording was conducted by irradiating a light to recording medium 1 with xenon lamp 15 and by applying again a voltage of +5 V to probe electrode 2. The recording medium was found to have transferred to an ON state in which the electricity flows well.

The light irradiation and the voltage application were stopped, and then at the same position, a voltage of +300 mV was applied to probe electrode 2 to reproduce the record. A current of 5 nA was found to flow, which shows the retention of the ON state, namely the retention of the record.

After stopping an application of the voltage, argon laser 16 was projected onto the recorded portion and vibration energy was given thereto. Thereafter at the same position, a voltage of +300 mV was applied again to probe electrode 2 to reproduce the record. A current of not more than 1 pA was found to flow, which shows the transition to an OFF state, namely erasure of the record.

## 40 Example 3

The recording-reproducing apparatus illustrated in Fig. 1 was employed in the same manner as in Example 1.

The film of octadecyltetracyanoquinodimethan silver complex (ODTCNQ/Ag) was formed in the following procedure. A solution of  $4 \times 10^{-6}$  M ODTCNQ/Ag in acetonitrile (ACN) was prepared. The solution was spread on pure water at 20 °C, and the surface pressure was raised to 15 mN/m to form a monomolecular film on the surface of water. A glass substrate having a vapor-deposited gold/palladium (Au/Pd) film of 300 Å thick which had been previously immersed in the water phase was slowly pulled up at a rate of 5 mm/min in the direction crossing the water surface with the surface pressure maintained constant to form a monomolecular film of ODTCNQ/Ag on the glass substrate having vapor-deposited Au/Pd. This was employed as recording medium 1.

The experiment on recording-reproducing-erasing was conducted by employing recording medium 1 having a monolayer LB film of the ODTCNQ/Ag. Firstly, recording medium 1 was placed on XY stage 14, and probe electrode 2 was fixed at a visually determined position. The distance Z between probe electrode 2 and the surface of recording layer 101 was adjusted by applying the voltage of 3 V between Au/Pd electrode 3 and the probe and by monitoring the current. On application of voltage of +300 mV to the probe electrode 2, the current was found to be not more than 1 pA.

After stopping an application of the voltage, the recording was conducted by irradiating a light to

recording medium 1 with a helium-neon laser in place of xenon lamp 15 and applying again a voltage of +3 V to probe electrode 2. The recording medium was found to have transferred to an ON state in which the electricity flowed well.

The light irradiation and the voltage application were stopped, and then at the same position, a voltage of +300 mV was applied to the probe electrode 2 to reproduce the record. A current of 5 nA was found to flow, which shows the retention of the ON state, namely the retention of the record.

After stopping an application of the voltage, a carbon dioxide laser in place of argon laser 16 was projected onto the recorded portion and vibration energy was given thereto. Thereafter at the same position, a voltage of +300 mV was applied again to probe electrode 2 to reproduce the record. A current of not more than 1 pA was found to flow, which shows the transition to OFF state, namely erasure of the record.

#### Example 4

The recording-reproducing apparatus illustrated in Fig. 1 was employed in the same manner as in Example 1.

The film of octadecyltricyanoquinodimethan silver complex (ODTCNQ/Ag) was formed in the following procedure. A solution of  $4 \times 10^{-6}$  M ODTCNQ/Ag in acetonitrile (ACN) was prepared. The solution was spread on pure water at 20°C, and the surface pressure was raised to 15 mN/m to form a monomolecular film on the surface of water. An n<sup>+</sup>-Si substrate which had been previously immersed in the water phase was slowly pulled up at a rate of 5 mm/min in the direction crossing the water surface with the surface pressure maintained constant to form a monomolecular film of ODTCNQ/Ag on the n<sup>+</sup>-Si substrate, which was employed as recording medium 1.

The experiment on recording-reproducing-erasing was conducted by employing recording medium 1 having a monolayer LB film of the ODTCNQ/Ag. Firstly, recording medium 1 was placed on XY stage 14, and probe electrode 2 was fixed at a visually determined position. The distance Z between probe electrode 2 and the surface of recording layer 101 was adjusted by applying the voltage of 3 V between electrode (n<sup>+</sup>-Si) 3 and the probe and by monitoring the current. On application of voltage of +300 mV to probe electrode 2, the current was found to be not more than 1 pA.

After stopping an application of the voltage, the recording was conducted by irradiating a light to recording medium 1 with helium-neon laser 15 and by applying again a voltage of +3 V to probe electrode 2. The recording medium was found to have transferred to an ON state in which the electricity flowed well.

The light irradiation and the voltage application were stopped, and then at the same position, a voltage of +300 mV was applied to probe electrode 2 to reproduce the record. A current of 5 nA was found to flow, which shows the retention of the ON state, namely the retention of the record.

After stopping an application of the voltage, carbon dioxide laser 16 was projected onto the recorded portion and vibration energy was given thereto. Thereafter at the same position, a voltage of +300 mV was applied again to probe electrode 2 to reproduce the record. A current of not more than 1 pA was found to flow, which shows the transition to OFF state, namely erasure of the record.

#### Example 5

Fig. 2 illustrates an example of another embodiment of the present invention. In the Fig., memory material 103 (described later) is adhered by the Langmuir-Blodgett process or other method onto electroconductive transparent electrode 102 such as ITO (indium-tin oxide) provided on glass plate 101. Further probe 104 is brought to proximity of approximately sub-nanometer to the desired position of the memory material by means of a probe-position-controlling means. Probe 104 is made of an electrolytically polished tungsten wire, a mechanically cut platinum wire, or the like having a sharp tip (a radius of curvature of less than 1 μm) and is electroconductive. Probe-position-controlling means 105 comprises such as a PTZ element and serves to move probe 104 to a desired position within a plane and the normal line direction in the memory area.

Writing/erasing is conducted in the following manner. Firstly, electromagnetic wave 108 is projected onto memory material 103 in the memory region through the glass substrate 101 and the transparent electrode by operating electromagnetic wave source 107 with lens 109 in accordance with the signal from writing/erasing signal generator 106.

Simultaneously the signal from writing/erasing signal generator 106 is sent to transparent electrode 102 to apply the electric field formed between transparent electrode 102 and probe 104 to the desired position

of memory material 103, thus writing or erasing being conducted.

Examples of the signals in writing are shown in Fig. 3A to Fig. 3C. Fig. 3A shows a signal given to probe-position-controlling means 105, by which probe 104 accesses the desired position in the memory region. Fig. 3B shows an electromagnetic-wave-source-operating signal. Fig. 3C shows a writing signal given to the memory material. The writing is conducted at a memory position where the two signals are given simultaneously (namely region M in Fig. 3).

Examples of signals in erasing are shown in Fig. 4A to Fig. 4C, which illustrate erasing in the region where the writing has been conducted in the process shown in Fig. 3. Fig. 4A and Fig. 4B are the same as Fig. 3A and Fig. 3B, and Fig. 4C shows an erasing signal given to the memory material. The erasing is conducted at a memory position where the two kinds of signals are given simultaneously (namely region E in Fig. 4).

Readout is conducted in the following manner. A bias voltage is applied by bias source 110 onto the memory material on transparent electrode 102, and tunnel current 111 flowing between memory material 103 and probe 104 which is in the proximity of sub-nanometer to memory material 103 is detected by means of current detecting circuit 112. The tunnel current intensity at a written portion (being in an ON state) is different from the intensity at a non-written portion or an erased portion (being in an OFF state) on memory material 103 because the electron distribution state on the surface and the inside of the memory material is different between the two state. This difference of the tunnel current intensity is treated with readout treating circuit 113 to provide a readout signal (ON-OFF signals).

Examples of signals in readout operation are shown in Fig. 3D and Fig. 4D. Fig. 3D shows the tunnel current signal detected, after writing is conducted as described referring to Fig. 3A to Fig. 3C, by scanning again the same region. In this example, the tunnel current increases at the portions corresponding to the written portions. Fig. 4D shows the tunnel current signal detected, after erasing is conducted as described by referring to Fig. 4A to Fig. 4C, by scanning again the same region.

The memory material employed in the present invention and the principle of writing/erasing therein are described below. As an example of the memory material, an azo compound is taken which has the structure shown in Fig. 5A (in which the positions of the quinone groups, and the hydroquinone groups include ortho, meta, and para positions). Irradiation to the compound with light of wavelength of 400 nm causes photoisomerization from the trans configuration to the cis configuration at the azo group in the molecule to give the structure shown in Fig. 5B. With the irradiation of the light maintained, the application of an electric field between transparent electrode 102 and probe 104 in the direction as shown in the figure causes proton ( $H^+$ ) transfer between the quinone group and the hydroquinone group, which are in a hydrogen-bonded state, giving the structure shown in Fig. 5C. On stopping the light irradiation, a photoisomerization occurs again from the cis configuration to the trans configuration to give the structure shown in Fig. 5D. This structure corresponds to the written state which is different from the structure of the initial state shown in Fig. 5A in the intramolecular electron distribution and is caused by the proton transfer between the hydroquinone group and the quinone group. As the result, the shape of the tunnel barrier between transparent electrode 102 and probe 104 changes corresponding to the structure as shown in Fig. 5A (the initial state) and the structure as shown in Fig. 5D (the written state), thus giving the change of the tunnel current intensity flowing under the application of the bias voltage between transparent electrode 102 and probe 104. The detection of this change enables the discrimination of the states of the molecules (the initial state and the written state) at the position, to which probe 104 is in access. An example of the detected tunnel current signals are shown in Fig. 3D, corresponding to the instance of Fig. 3A to Fig. 3C in which the tunnel current rises at the portion in the written state in comparison with the initial state.

The erasing of the written state of the memory material shown in Fig. 5 is explained in reference to Fig. 6. Irradiation with light of wavelength of 400 nm onto the compound having the structure shown in Fig. 6A in a written state causes photoisomerization of the compound from the trans configuration to the cis configuration at the azo group in the molecule to give the structure shown in Fig. 6B. With the light irradiation maintained, the application of an electric field between transparent electrode 102 and probe 104 in the direction shown in Fig. 6C (in the direction reverse to that shown in Fig. 5C) causes proton ( $H^+$ ) transfer between the quinone group and the hydroquinone group which are in a hydrogen-bonded state, giving the structure shown in Fig. 6C. On stopping the light irradiation, the photoisomerization occurs again from the cis configuration of the trans configuration to give the structure shown in Fig. 6C. This structure corresponds to an erased state which is the same as the initial state shown in Fig. 5A. The erasing of the written state is conducted in such a manner. An example of the detected tunnel current is shown in Fig. 4D corresponding to Fig. 4A to Fig. 4C. In the position where once writing was conducted and then erasing has been conducted, the tunnel current falls to the same value as that at the initial state.

The experiments of recording-reproducing-erasing were repeatedly conducted with the memory material

shown in Fig. 5 and Fig. 6 by employing the apparatus having the constitution as shown in Fig. 2 in the same manner above. The result showed that recording/erasing could be made at least approximately 100 times of repetition without deterioration of the memory material and the reproduction without causing the change of the recording-erasing state.

The memory materials employed in the present invention are those capable of undergoing photoisomerization between a trans configuration and a cis configuration (or between a syn configuration and an anti-syn configuration) on light irradiation. Such materials include those having a carbon-carbon double bond or an imino group in addition to the material employed in the above examples having an azo group. The redox pair undergoing proton transfer on application of an electric field includes a hydrogen bonding system of amino group-amino group in addition to the hydrogen bonding system of quinone group-hydroquinone group employed in the above examples.

As described above, the recording-reproducing apparatus of the present invention which is based on the principle of STM can conduct recording and erasing by electromagnetic wave irradiation and electric field application on a memory material, and conduct reproduction by tunnel current detection, so that it enables a large capacity of recording and reproducing without change of record at reproduction with reproducibility and stability. With a bit size of 10 nm for the recording, a large capacity of a recording-reproducing apparatus of as large as  $10^{12}$  bit/cm<sup>2</sup> is achievable.

Further, the present invention has the advantages as follows: The formation of a monomolecular film in the present invention according to an LB process can give a film having an excellent order of the molecules and a high density, which is suitable for super-high-density recording media. An erroneous writing is prevented at the time of reproduction because recording is conducted under irradiation of light. The storage stability is excellent because erasing of a record requires a vibration energy to be given.

## Claims

1. A recording-reproducing apparatus, comprising a material, in which an intramolecular electron distribution can be changed, by electromagnetic wave irradiation and electric field application, a probe electrode brought close to the material, a means for projecting an electromagnetic wave onto the material, and a means for applying an electric field between the material and the probe electrode.

2. The recording-reproducing apparatus of Claim 1, wherein the apparatus comprises a means for applying a bias voltage between the probe electrode and the material, and a means for detecting current flowing between the probe electrode and the material.

3. The recording-reproducing apparatus of Claim 1, wherein said material is deposited on an electrode according to the Langmuir-Blodgett process.

4. A recording-reproducing apparatus, comprising a recording medium, in which a material capable of causing a proton-transfer by photoisomerization is deposited on an electrode; a probe electrode brought close to the recording medium; a means for projecting an electromagnetic wave onto the recording medium; and a means for applying electric field between the recording medium and the probe electrode.

5. The recording-reproducing apparatus of Claim 4, wherein the material is selected from the group of compounds consisting of azo compounds, styrene derivatives and imino compounds having a quinone group and hydroquinone group in the molecule, and azo compounds, styrene derivatives and imino compounds, styrene derivatives and imino compounds having two amino groups in the molecule.

6. The recording-reproducing apparatus of Claim 4, wherein the apparatus comprises a means for applying a bias voltage between the probe electrode and the material, and a means for detecting current flowing between the probe electrode and the material.

7. The recording-reproducing apparatus of Claim 4, wherein the recording medium is deposited on the electrode according to the Langmuir-Blodgett process.

8. A recording-reproducing apparatus, comprising a recording medium, in which a charge transfer complex is deposited on an electrode, a probe electrode brought close to the recording medium, a means for projecting light onto the recording medium, and a means for applying electric field between the recording medium and the probe electrode.

9. The recording-reproducing apparatus of Claim 8, wherein the charge transfer complex is composed of a metal or a metal ion and an organic electron acceptor.

10. The recording reproducing apparatus of Claim 9, wherein the charge transfer complex is selected from the group consisting of n-octadecyltetracyanoquinodimethan copper complex (ODTCNQ/Cu), n-dodecyltetracyanoquinodimethan copper complex (DDTCNQ/Cu), n-octadecyltetracyanoquinodimethan silver complex (ODTCNQ/Ag), n-dodecyltetracyanoquinodimethan silver complex (DDTCNQ/Ag), and their

derivatives.

11. The recording-reproducing apparatus of Claim 8, wherein a monomolecular film of the charge-transfer complex is deposited on the electrode.

12. The recording-reproducing apparatus of Claim 8, wherein the apparatus comprises a means for  
5 applying a bias voltage between the probe electrode and the recording medium, and a means for detecting current flowing between the probe electrode and the recording medium.

13. A recording method comprising projecting an electromagnetic wave and simultaneously applying  
10 electric field onto a material, in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application to cause change in the electron distribution in the molecule of the material to write information, thereby conducting information-recording.

14. A recording-reproducing method, comprising conducting information-recording by projecting an  
15 electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application thereby causing change in the electron distribution in the molecule of the material to write information; and conducting information readout by detecting a current at the portion where the information is recorded.

15. A recording-reproducing-erasing method, comprising conducting information-recording by projecting  
20 an electromagnetic wave and simultaneously applying electric field onto a material in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application thereby causing change in the electron distribution in the molecule of the material to write information; conducting information readout by detecting a current at the portion where the information is recorded; and erasing the information by projecting an electromagnetic wave and simultaneously applying electric field onto the portion where the information is recorded.

16. A recording-reproducing-erasing method, comprising conducting information-recording by projecting  
25 an electromagnetic wave and simultaneously applying electric field onto a material, in which intramolecular electron distribution can be changed, by electromagnetic wave projection and electric field application thereby causing change in the electron distribution in the molecule of the material to write information; conducting information readout by detecting a current at the portion where the information is recorded; and erasing the information by introducing a vibration energy to the portion where the information is recorded.

17. A recording medium, comprising providing a material capable of causing a proton-transfer by  
30 photoisomerization on a substrate.

18. The recording medium of Claim 17, wherein the material is selected from the group of compounds consisting of azo compounds, styrene derivatives and imino compounds having a quinone group and hydroquinone group in the molecule, and azo compounds, styrene derivatives and imino compounds having two amino groups in the molecule.

19. The recording medium of Claim 17, wherein a monomolecular film or its laminated film is formed on  
35 a substrate.

20. A recording medium comprising a substrate carrying a compound which can be converted into different isomers by non-chemical means to alter the response of the medium to an external electric field.

21. A recording medium comprising a substrate carrying a compound which is in first and second  
40 states of different electron distribution in different regions, data being recoverable by scanning the medium and determining the state of the regions.

22. A reproducing apparatus comprising a compound having states of different intramolecular electron distribution between which it can be altered by non-chemical means and means for scanning the medium to  
45 determine the state of the compound.

50

55

60

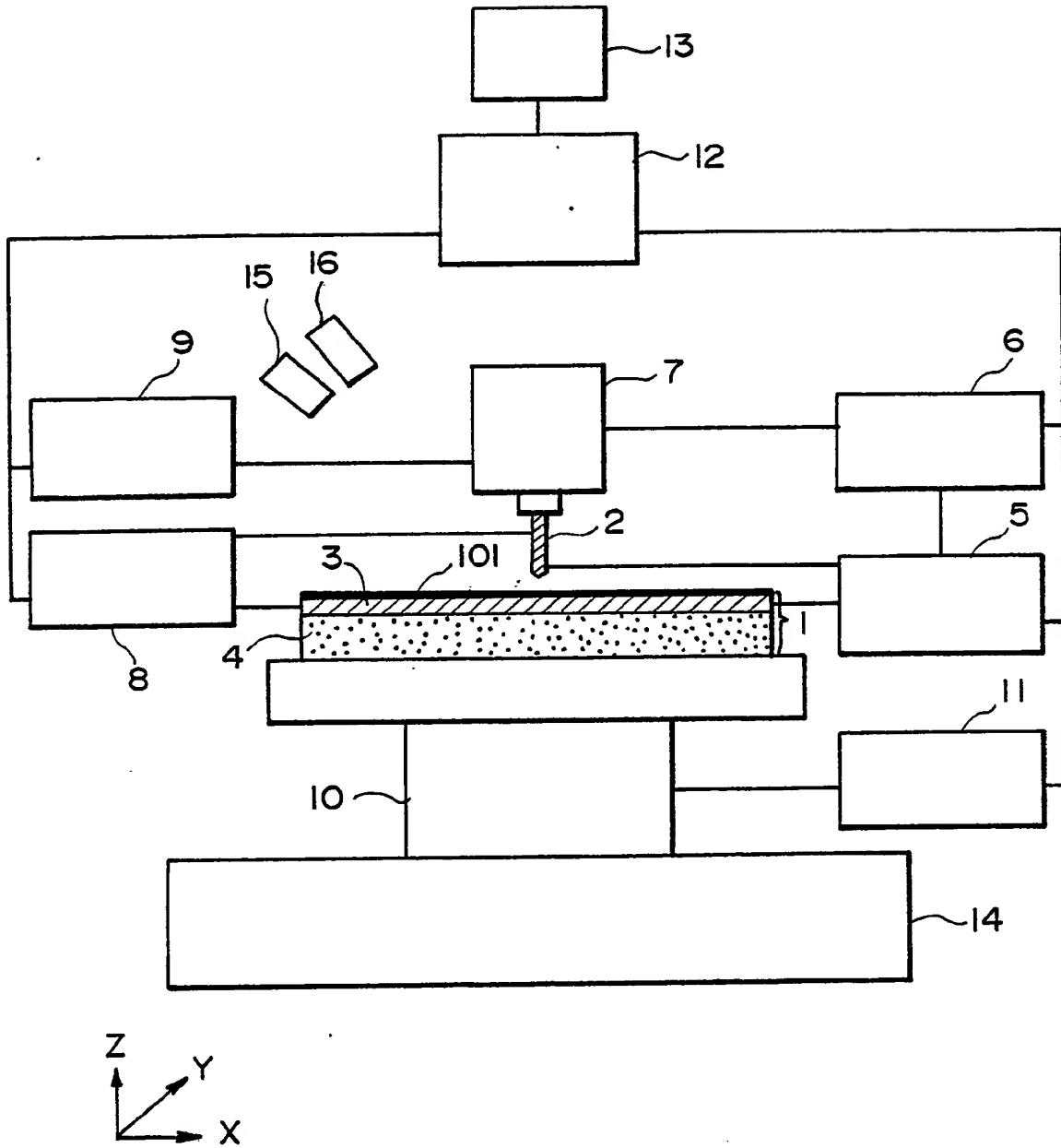


FIG. 1

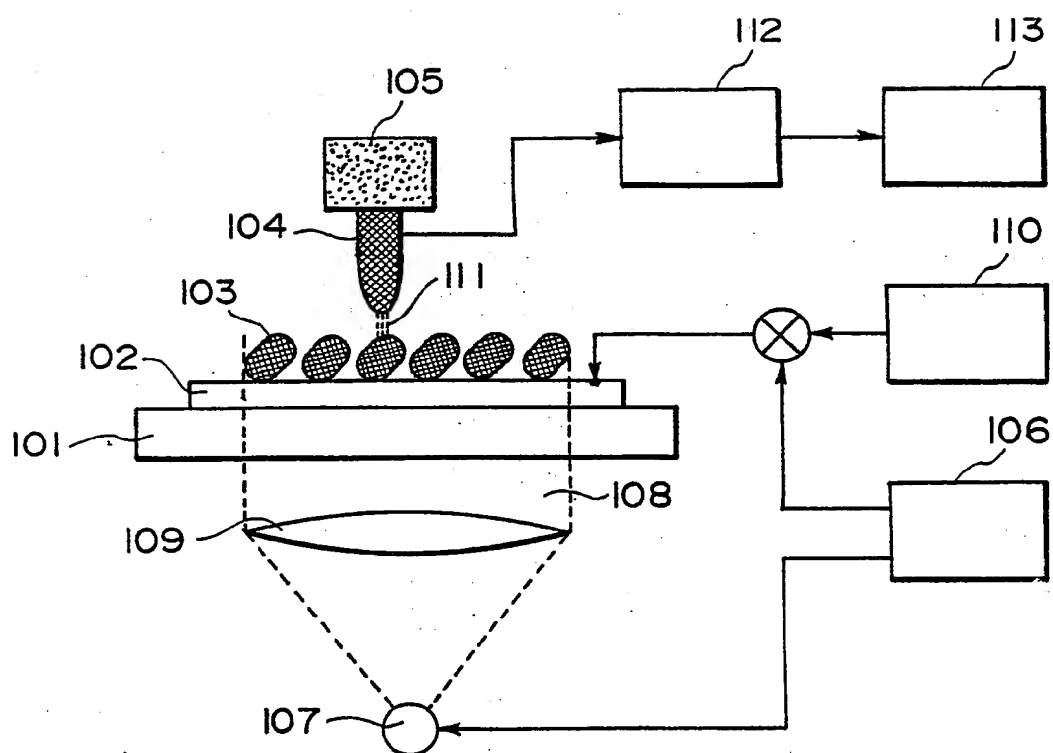


FIG. 2



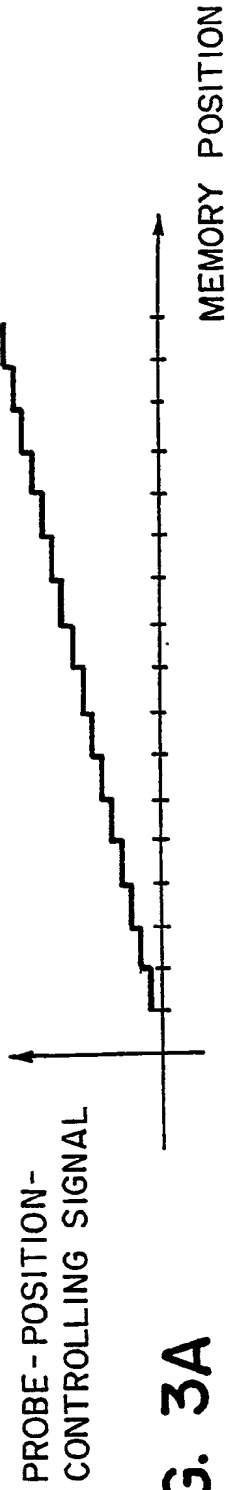


FIG. 3A

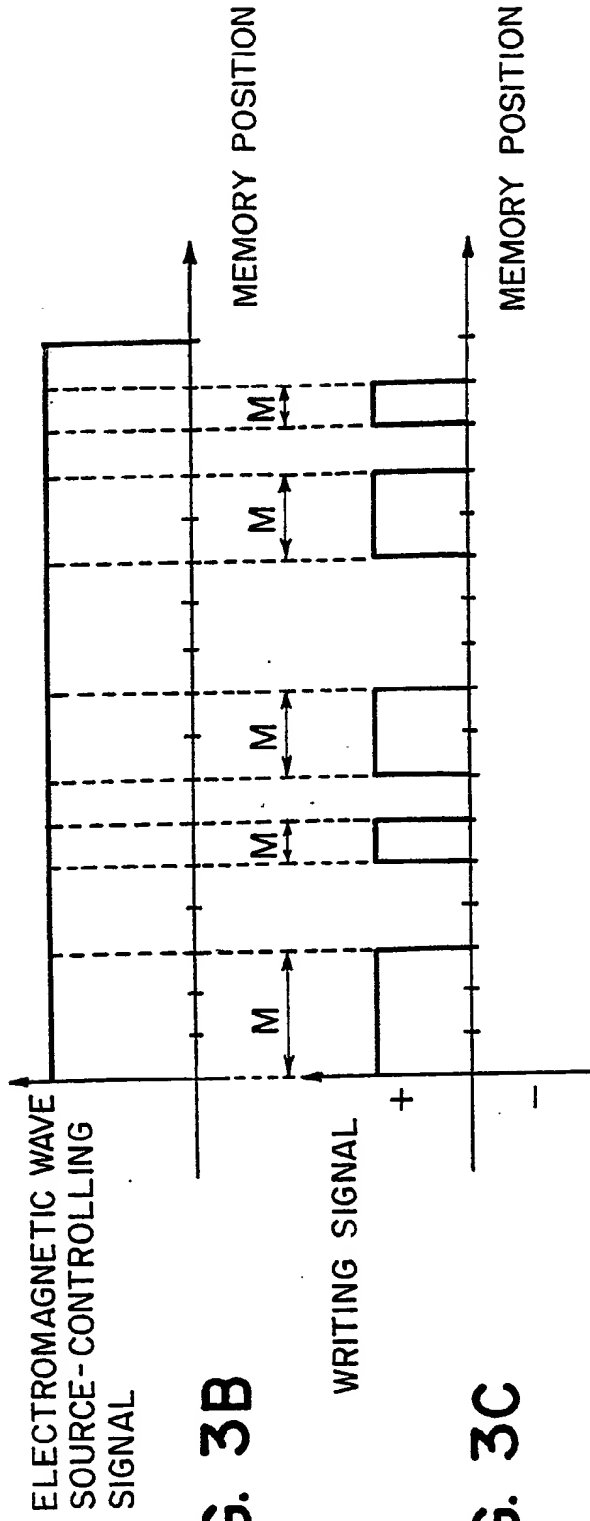


FIG. 3B

FIG. 3C

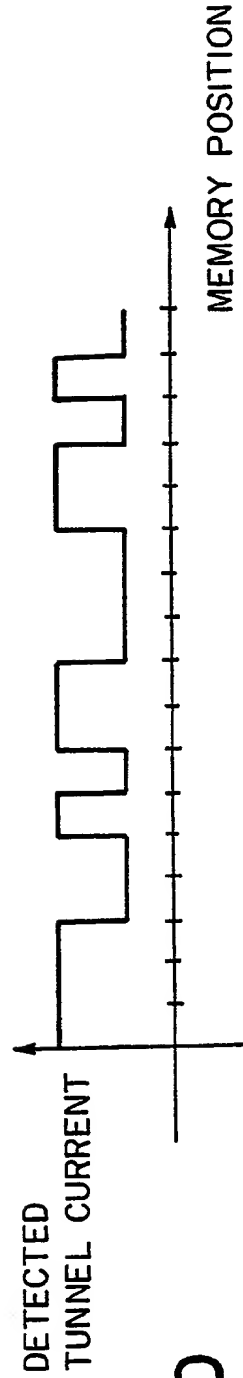
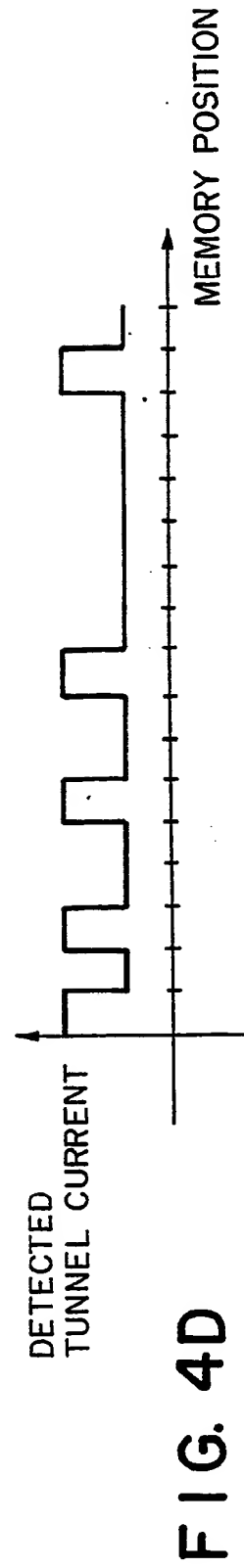
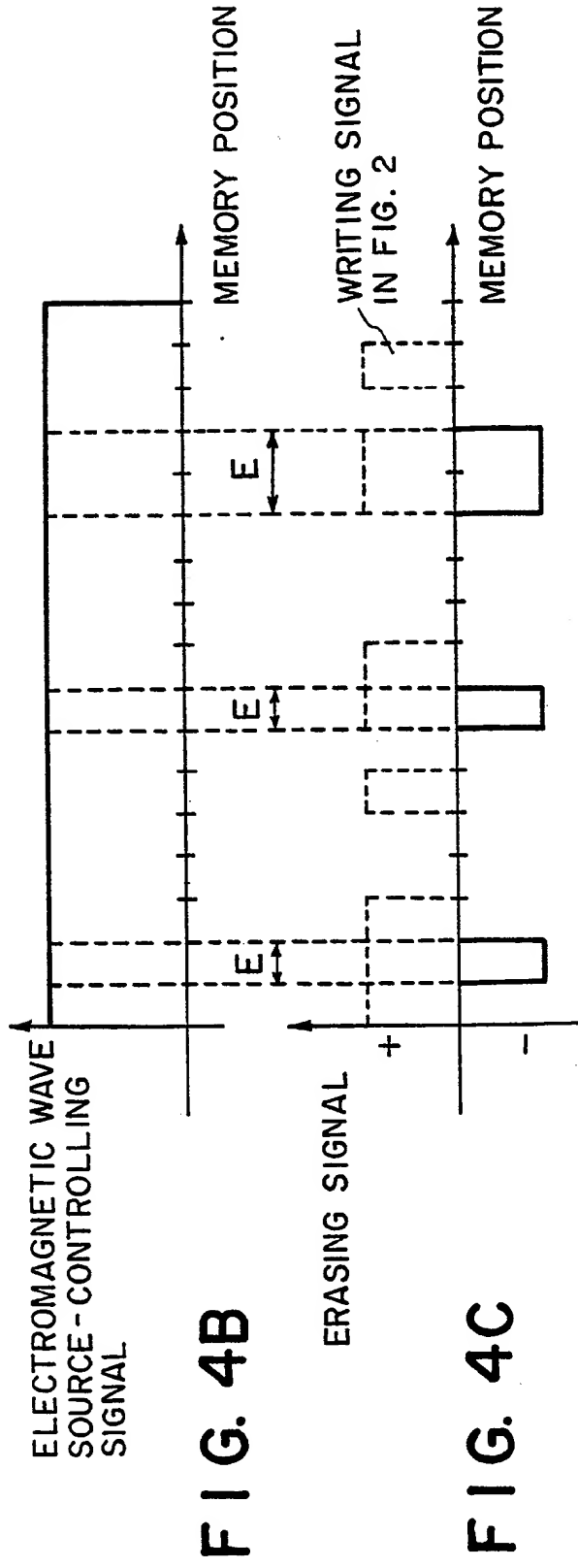
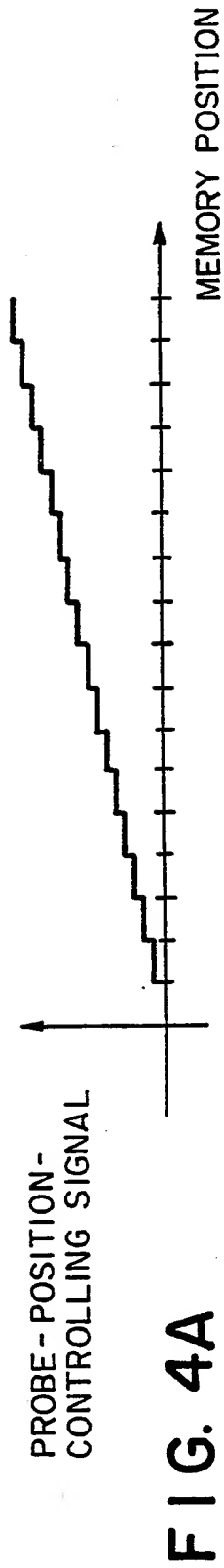


FIG. 3D



INITIAL STATE

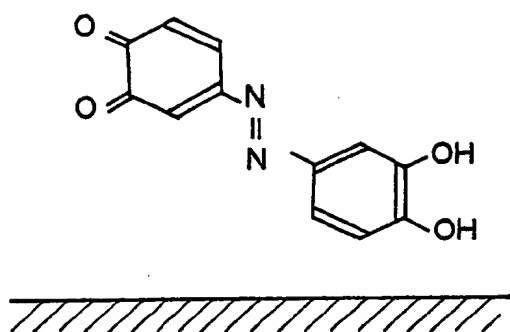


FIG. 5A

LIGHT IRRADIATION

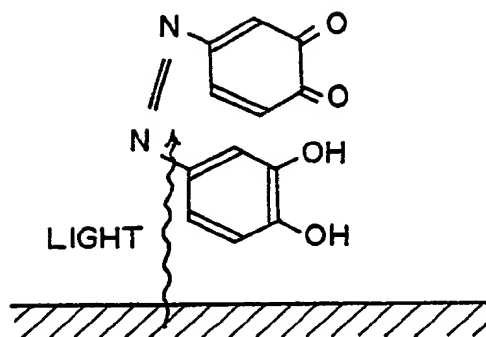


FIG. 5B

LIGHT IRRADIATION  
& ELECTRIC FIELD APPLICATION

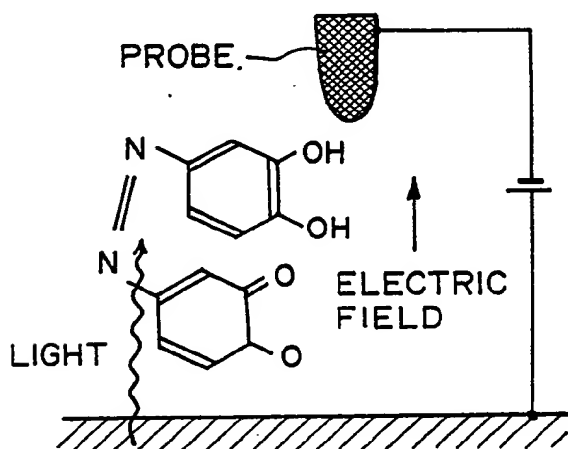


FIG. 5C

WRITTEN STATE

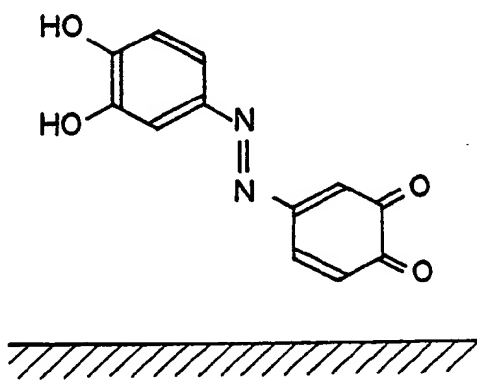


FIG. 5D

WRITTEN STATE

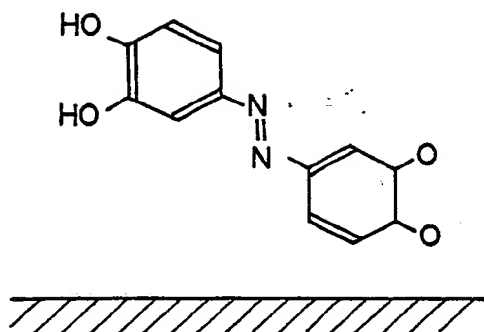


FIG. 6A

LIGHT IRRADIATION

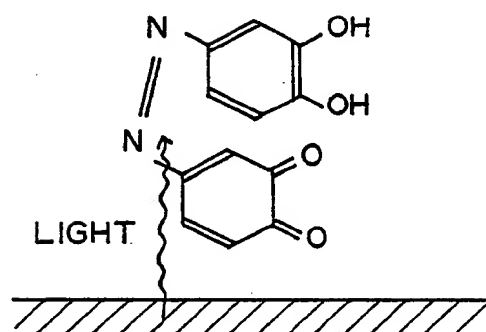


FIG. 6B

LIGHT IRRADIATION & REVERSE ELECTRIC FIELD APPLICATION

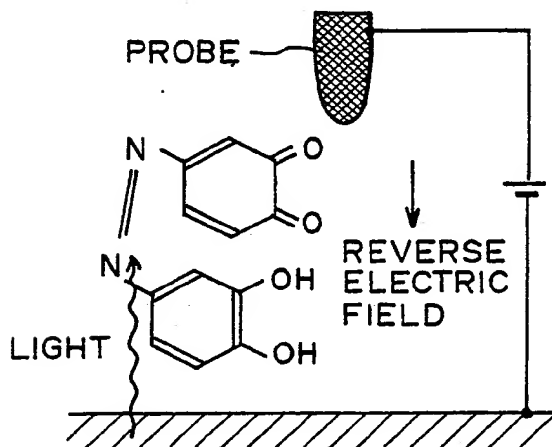


FIG. 6C

ERASED STATE (INITIAL STATE)

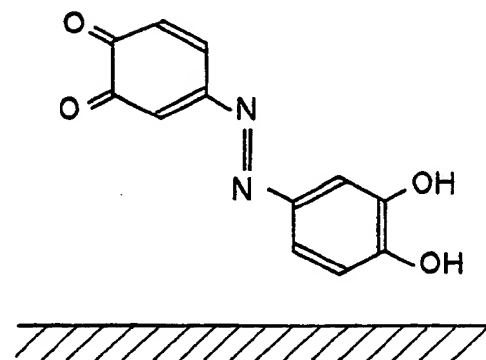


FIG. 6D

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 363 147 A3**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **89310092.5**(51) Int. Cl.<sup>5</sup>: **G11B 9/00**(22) Date of filing: **03.10.89**

(30) Priority: **04.10.88 JP 251455/88**  
**01.12.88 JP 302223/88**

(43) Date of publication of application:  
**11.04.90 Bulletin 90/15**

(84) Designated Contracting States:  
**AT BE CH DE ES FR GB GR IT LI LU NL SE**

(88) Date of deferred publication of the search report:  
**17.07.91 Bulletin 91/29**

(71) Applicant: **CANON KABUSHIKI KAISHA**  
**30-2, 3-chome, Shimomaruko, Ohta-ku**  
**Tokyo(JP)**

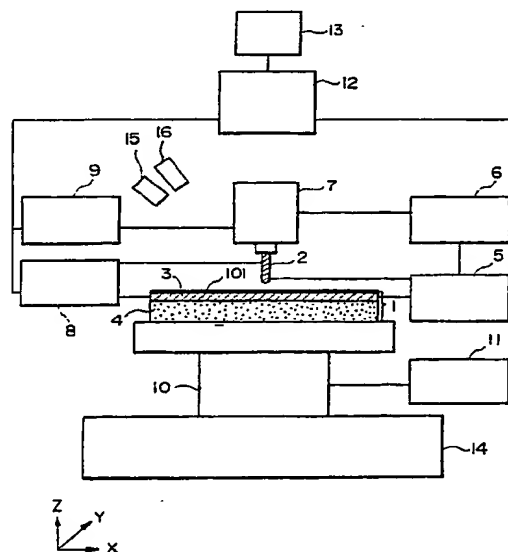
(72) Inventor: **Kawada, Haruki**

**48-1-1-208, Kamadai Hodogaya-ku**  
**Yokohama-shi Kanagawa-ken(JP)**  
Inventor: **Matsuda, Hiroshi**  
**17-2, Higashi Naruse Isehara-shi**  
**Kanagawa-ken(JP)**  
Inventor: **Takimoto Kiyoshi**  
**2-13-202, Kuriya 4-chome Tama-ku**  
**Kawasaki-shi Kanagawa-ken(JP)**  
Inventor: **Nose, Hiroyasu**  
**4731-1-204, Sobudai 3-chome Zama-shi**  
**Kanagawa-ken(JP)**

(74) Representative: **Beresford, Keith Denis Lewis**  
**et al**  
**BERESFORD & Co. 2-5 Warwick Court High**  
**Holborn**  
**London WC1R 5DJ(GB)**

(54) **Recording and reproducing apparatus and recording and reproducing method and recording medium for the recording and reproducing method.**

(57) A recording-reproducing apparatus, comprising a material (1), in which an intramolecular electron distribution can be changed, by electromagnetic wave irradiation and electric field application, a probe electrode (2) brought close to the material, a means (15) for projecting an electromagnetic wave onto the material, and a means (8) for applying an electric field between the material and the probe electrode, is provided.

**FIG. 1****EP 0 363 147 A3**



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 89 31 0092

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	EP-A-0 238 759 (K.K. TOSHIBA) * the whole document *	1-5,7,13, 17-19, 20-22, 8-12, 14-16	G 11 B 9/00 G 11 B 13/00 G 11 B 9/04 G 11 B 11/08
Y,A	EP-A-0 272 935 (CANON K.K.) * the whole document *	8-12, 14-16, 1-7,13, 17-22	
A	DE-A-3 607 932 (W. KREUTZ) * the whole document *	1,2,4,21, 22	
A	WO-A-8 403 169 (THE JOHN HOPKINS UNIVERSITY) * the whole document *	4,5,8-10, 17,18, 20-22	
A	EP-A-0 073 304 (I.B.M. CORP)		
P,X,P,A	IBM TECHNICAL DISCLOSURE BULLETIN. vol. 32, no. 2, July 1989, ARMONK, N.Y., USA pages 285 - 286; "INFORMATION STORAGE WITH SCANNING TUNNELING MICROSCOPE" * the whole document *	20-22,1, 2,4-6,17-	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  G 11 B G 11 C
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		15 April 91	FUX J.
<b>CATEGORY OF CITED DOCUMENTS</b> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention  E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family, corresponding document			